(19) Japan Patent Office (JP)

(11) Patent Application Publication No.

H01-179471

(12) Patent Application Publication (A)

(43) Publication Date: July 17, 1989

(51) Int. Cl.[4]	Classification symbol	Internal reference No.
H 01 L 33/00		A-7733-5F

Examination request: Requested

Number of claims: 2 (Total 3 pages)

---

(54) Invention Title:

P-N Junction Light Emitting Device Made of Cubic Boron Nitride

(21) Application No.: S63-1605

(22) Application Date: Jan. 7, 1988

(72) Inventor: Osamu Mishima 4-914-203 Namiki, Tsukubashi
Ibaraki-kenn

(72) Inventor: Akira Era 1-13-12 Senmgenn, Tsukubashi
Ibaraki-kenn

(72) Inventor: Junzou Tanaka 2-803-203 Azuma, Tsukubashi
Ibaraki-kenn

(72) Inventor: Osamu Mishima 3-14-10 Nihomiya, Tsukubashi
Ibaraki-kenn

(71) Applicant: Chief of Inorganic Materail Labs
the Science and Technology Agency
1-1 Namiki, Tsukubashi, Ibaraki-kenn

Specification

1. Invention Title:

P-N Junction Light Emitting Device Made of Cubic Boron Nitride

2. What is Claimed is:

1) A light emitting device made of a device having a p-n junction employing cubic boron nitride as a mother crystal.

2) A light emitting device in which a phosphor is provided at a p-n junction section or on its n-side surface of a device having a p-n junction employing cubic boron nitride as a mother crystal.

3. Detailed Explanation of the Invention

Field of Industrial Application

The present invention relates to a light emitting device. In further detail, it relates to a light emitting device which employs cubic boron nitride as a mother crystal and which can emit light in a wide range of infrared to UV.

Conventional Technologies

Conventionally, gallium arsenide and gallium phosphide are known and put into practice as materials for making up p-n junction light emitting devices. The emission ranges of these light emitting devices, however, span from infrared to ultraviolet regions. Silicon carbide and zinc selenide have been developed as materials for devices to provide blue emissions. It is difficult, however, to obtain silicon carbide with excellent quality and to prepare p-type crystals with zinc selenide, making it difficult to obtain a p-n junction. Therefore, their devices are not put into practical use. Moreover, gallium

nitride and zinc sulfide which have a band gap corresponding to the ultraviolet region can not be prepared in p-type and their p-n junction light emitting devices in UV region do not exist.

Purpose of the Invention

The present invention intends to provide light emitting devices which can provide an emission in the infrared to UV regions, which was difficult or impossible to achieve when conventional p-n junction light emitting devices are employed.

Constitution of the Invention

As a result of dedicated research to achieve the above purpose, the present inventors were able to confirm that emissions in the infrared to the UV regions were obtained when a current was flown through a p-n junction section of p-n junction devices employing cubic boron nitride as a mother crystal and that these devices are excellent light emitting devices. Moreover, the present inventors found that a phosphor placed on the p-n junction section or on the surface of its n-side can alter the emission to any color. Based on these pieces of knowledge, the present inventors have completed the present invention.

The essence of the present invention lies in

1) A light emitting device made of a device having a p-n junction employing cubic boron nitride as a mother crystal; and

2) A light emitting device in which a phosphor is provided at a p-n junction section or on its n-side surface of a device having a p-n junction employing cubic boron nitride as a mother crystal.

The device having a p-n junction employing cubic boron nitride as a mother crystal can be produced according to the following method.

A high and low temperature zones are prepared in a vessel sealed under a high pressure and high temperature made of a material such as molybdenum. Cubic BN source pieces and a p- or n-type dopant are dissolved in their solvent such as lithium calcium nitride (LiCaBN2) solvent and the melt is introduced into the high temperature

zone. A cubic boron nitride crystal substrate with a type opposite to the above dopant type is placed in the low temperature zone. Utilizing a difference in the solubility between different temperatures, cubic boron nitride with a conductivity which is different from that of the crystal substrate which is placed in the low temperature zone precipitates and grows. Thus, a p-n junction device is obtained. The growth can be conducted under a vessel pressure of 4 ~ 7GPa and temperatures of 1,300 ~ 2,400°C. A preferred pressure is 5.5GPa and temperature is about 1,700°C.

An example of an n- and p-type dopant are silicon and beryllium, respectively. A very small junction area produces a weak emission. Therefore, a preferred junction area is 0.3 mm^2. There is no restriction on the size and shape of a mother crystal. The crystal may be a chunk or a thin film in the shape. When a current flows through this p-n junction, recombination of electrons and holes in the vicinity of the p-n junction produces an emission. A zero current does not produce any emission, while a larger current produces a stronger emission. For a device with a p-n junction of about 1mm in area, a current of 1mA or larger is preferably flown. In order to flow a current across a p-n junction, an electrode shall be attached on a p- and n-type side and then, a current can flow between the electrodes. A current ordinarily flows from the p-type to n-type side. An emission occurs, however, even in a reverse direction.

The emission can occur, not only in wavelengths longer than red, but across a range including the red to ultraviolet region.

A phosphor placed on the p-n junction section or on a surface of the n-side can alter the emission color.

Example 1

Preparation of p-Type Cubic Boron Nitride Crystal Substrate

325 ~ 400 Mesh cubic boron nitride particles and LiCaBN solvent powder were placed within a growth vessel made of molybdenum (an inner diameter of 4mm, an inner height of 3mm and a thickness of 1mm). At this time, the solvent contained 1% by weight of metallic beryllium powder. The aforementioned growth vessel made of molybdenum is designed to maintain a temperature difference between a high and low temperature zone. The high temperature zone was pressurized to 5.5GPa and heated to

1,700°C, which were maintained for 20 hours. Thus, a p-type cubic boron nitride crystal substrate was obtained in the low temperature zone.

P-N Junction

The above p-type cubic boron nitride crystal substrate was placed as a seed crystal in the low temperature zone of the growth vessel. The same cubic boron nitride particles as above and LiCaBN2 solvent powder containing 5% by weight of silicon particles were placed in the vessel. Under the same conditions as above, a growth was conducted and thereby, an n-type single crystal was grown on the p-type crystal. This p-n junction crystal was a single crystal with an overall size of approximately 1mm. Its center section was dark blue and of p-type and the surrounding section was made of an n-type crystal with a transparent orange color.

As illustrated in Figure 1, electrodes 4 made of silver paste were made on a p- and n- type section across the p-n junction. When a forward bias of 70 volts was applied with a positive on the p-type side and a negative on the n-side, a current of 2 mA flew from the p- to n-type side. The voltage between the p- and n-type sections across the p-n junction with voltage drops between the cubic boron nitride semiconductor and silver paste electrodes were excluded was approximately 5 volts across a distance of approximately 0.2mm. When the p-n junction device was observed under a real image microscope during the current of 2mA flew, a bluish white emission was observed on the n-type side along and vicinity of the p-n junction section.

Example 2

When a reverse bias of 70 volts was applied in Example 1, the voltage between the p- and n-type sections across the p-n junction was -40 volts and a current of 0.5 mA flew from the n- to p-type side. The n-type section was bright with orange emission.

Example 3

As the current was varied in Example 1, the emission intensity was measured using a photometer, which found that the emission intensity increased as the current increased. A few mA of current produces an emission which naked eyes can observe.

Example 4

Under the conditions in Examples 1 and 2, the emission spectrum was observed using a spectrometric photometer. The results are as illustrated in Figure 2. The figure shows raw data without calibrations for the measurement systems' sensitivity. As illustrated in the results, it was confirmed that the emission takes place even in a range of ultraviolet at 2,000 Angstroms to blue. Moreover, as the current increased, the emission range expanded toward shorter wavelengths.

Furthermore, emissions were not detected when a current flew through devices made of solely a p- or n-type material.

Example 5

On the p-n junction section or the surface of the n-side of the devices in Example 1, a phosphor, silver doped zinc sulfide, cupper doped zinc sulfide or europium doped yttrium oxysulfide, was applied. A forward current was flown through the p-n junction. Then, blue, green or red emission was observed, respectively.

Advantages of the Invention

The present invention can facilitate a p-n junction light emitting device which can produce an emission in a range of blue to ultraviolet, which a p-n junction light emitting device employing conventional materials can not accomplish. Further, cubic boron nitride is employed as a mother crystal and therefore, the device is superior to conventional one in the thermal conductivity, hardness and chemical stability. Thus, the present invention also has an advantage in that the device can be utilized under harsh environments such as a high temperature.

4. Brief Explanation of the Invention

Figure 1 depicts an example of a light emitting device of the present invention. Figure 2 illustrates a spectrum obtained in Example 4.

1:	n-Type	2:	p-Type
3:	p-n Junction surface	4:	Electrode

Patent Applicant: Chief of Inorganic Materail Labs
the Science and Technology Agency

Nobuo Sedaka

Figure 1

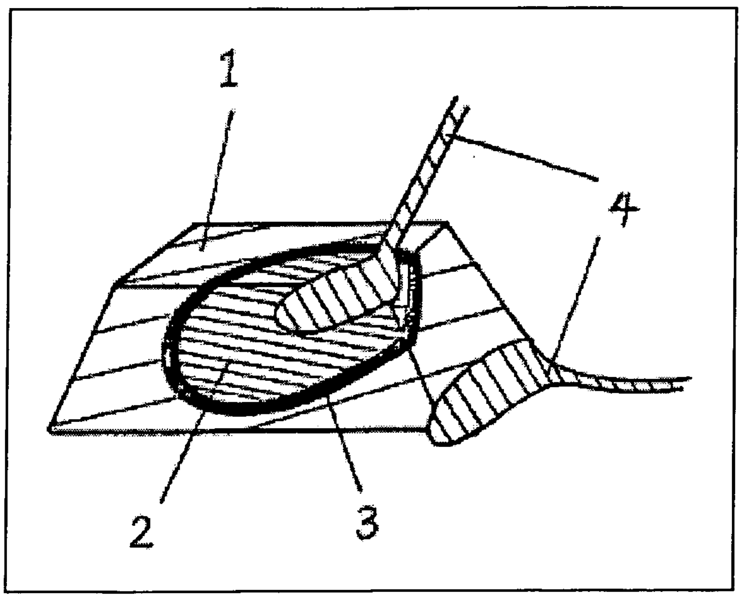
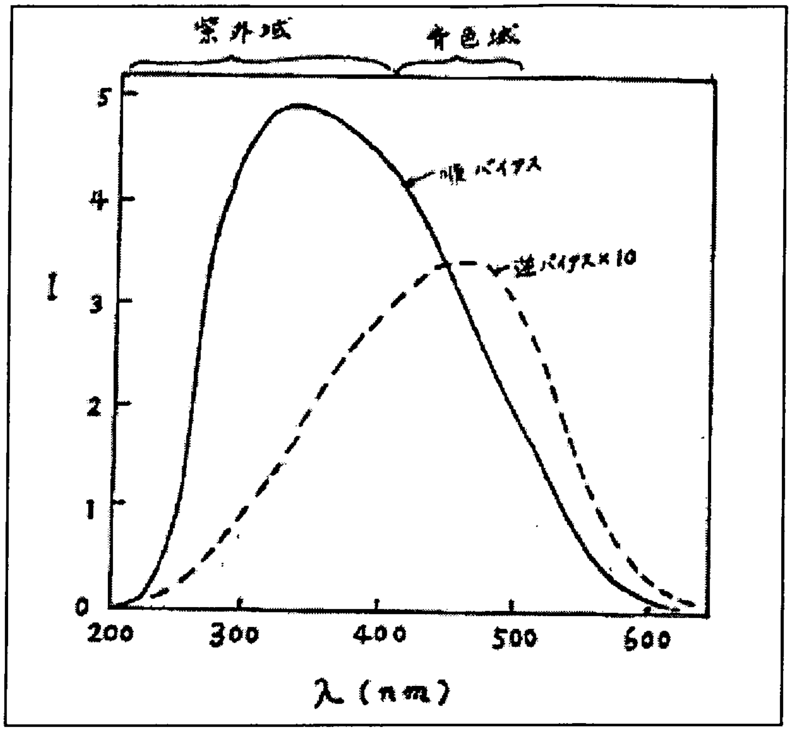


Figure 2

UV region Blue region



Forward bias

Reverse bias x 10